

YALE UNIV NEW HAVEN CONN DEPT OF ENGINEERING AND AP--ETC F/6 20/5
CALCULATIONS OF ATOMIC COLLISIONS RELEVANT TO GAS LASERS.(U)
APR 80 N00014-75-C-0559

N00014-75-C-0559
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LEVEL II

9 Final Report to ONR
On Contract N00014-75-C-0559

6 "Calculations of Atomic Collisions Relevant to Gas Lasers"

1/1/75 - 2/15/80

11 [23 April 1980

Abstract

The work done under the contract falls under three headings:

(1) 1975-76.

Vibrational transitions of molecules under electron impact, important in infrared lasers.

(2) 1977-79.

Interactions of electrons with polar molecules important in excimer lasers.

(3) 1977-79.

Interactions of electrons with noble gas atoms important in excimer lasers.

During the tenure of the contract,

(a) Five papers were published in Physical Review and Phys. Rev. Letters.

(b) Three invited papers were presented at international conferences.

(c) Two graduate students did their Ph.D. thesis work, and moved on to be postdocs in the field.

(d) Material for another three papers was produced, and is now waiting to be written up.

The total amount spent was \$163,000.

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NEW YORK, NEW YORK 10003

FEW:bg In reply, refer to:
7300/N00014-75-C-0559
Ser NY 694
23 April 1980

From: Administrative Contracting Officer, ONR Residency, New York City
To: Dr. I. Rowe, ONR, New York Area Office

Subj: Contract N00014-75-C-0559 w/Yale University

Encl: (1) 5 copies of Final Report, "Calculations of Atomic Collisions
Relevant to Gas Lasers, 1/1/75 - 2/15/80."

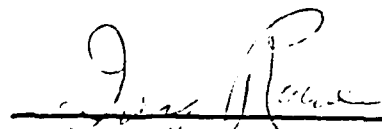
1. Enclosure (1) is submitted as the final technical report for the subject contract.
2. In anticipation of receipt of the Contractor's completion voucher under the subject contract, it is requested that the certificate below be executed, if appropriate, and that a signed copy thereof be returned to this office as soon as possible in order that further closeout actions will not be unduly delayed.


F.E. WALTERS

FIRST ENDORSEMENT on ONR Resident Representative ltr 7300/N00014-75-C-0559
dtd 23 April 1980 Ser NY 694

From:
To: ACO, ONR Residency, New York City

1. Returned.
2. The undersigned hereby certifies that the Contractor has completed the technical performance required under contract.

Name  Date 23 April 80
Title Deputy Resident for Science

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- §1.3 $e + N_2(v=0, v) \rightarrow e' + N_2(v=0, v')$; (Absolute cross-section calculation) -----

Interaction of electrons with polar molecules important in gas lasers

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(electron impact excitation of metastable and UV radiating states near threshold, through resonances with the "grandparent model").

List of publications -----

List of conference reports -----

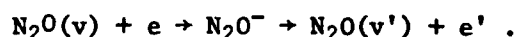
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§1.1 Vibrational excitation of a molecule by an electron at a resonance : the case of a lifetime too short for nuclear relaxation during the collision

(Publication 1).

This was the first calculation of vibrational excitation in a triatomic molecule at a resonance. There is an intermediate N_2O^- ion, which decays by autoionization to leave the residual molecule in a vibrationally excited state:



The resonance in question occurs at 2.3 eV of incident energy, and is about 0.7 eV broad (Fig. 1.1/1). Four parameters are used to describe the potential curves of the N_2O^- ion; between them, they account for the absolute cross-sections observed for the excitation of 19 different vibrational states (Fig. 1.1/2).

From the point of view of a gas-laser theorist, the importance of the paper lies in its demonstration that a theory of vibrational excitation with a small number of parameters (4 in this case) can account for a large number of cross-sections for vibrational change induced by electron impact, even in a target as complicated as a triatomic molecule.

§1.2 Vibrational excitation of a molecule by an electron at a resonance : the case of a lifetime long enough for some nuclear relaxation during the collision.
(Publication 2).

The vibrational excitation of N_2 molecules by electron impact at the 2 eV ($^2\Pi_g$) resonance is important in the pumping of N_2 -CO₂ lasers. Optimization calculations need not only the cross-sections for processes starting with the ground state, $v=0$, which can be measured in the laboratory, but also

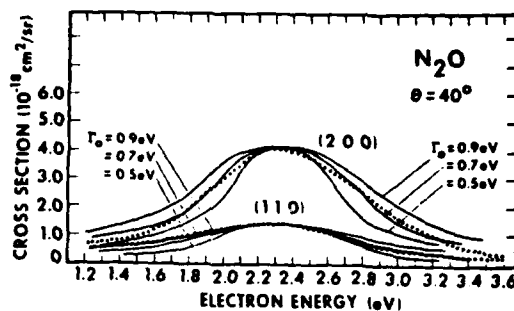


FIG. 1. Energy dependence of the differential cross sections for two different energy-loss processes. Experiment, dotted line; theory, solid line. The theoretical curves correspond to the parameters η_{ss} , η_{AS} , and B given in Sec. IX. As Γ_0 increases, so does the cross section both above and below the maximum.

Fig. 1.1/1 (From publication 1.)

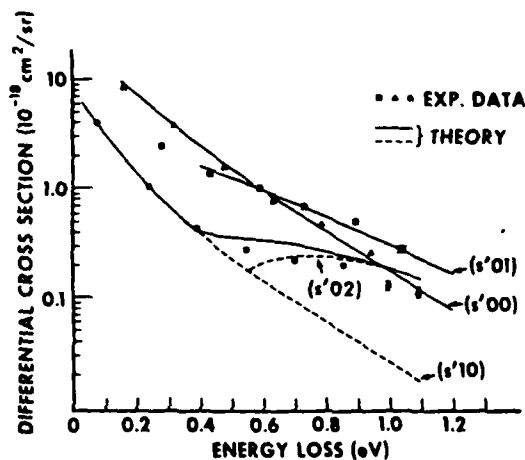
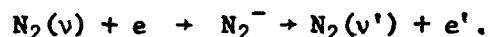


FIG. 2. Magnitude of differential vibrational cross sections at 40° vs energy loss. Experiment: \blacksquare , \blacktriangle , \bullet ; theory: solid line. The notation $s'b'a'$ is explained at the end of Sec. IV. For the sake of clarity, the theoretical points have been joined by continuous curves. The excitations $(s'02)$ and $(s'10)$ are accidentally degenerate within the experimental resolution for energy losses exceeding 0.4 eV; the broken curves are the calculated cross sections for these two excitations separately. The sum of these broken curves is shown as a continuous curve above 0.4 eV.

Fig. 1.1/2 (From publication 2.)

the transition cross-sections $v \rightarrow v'$ ($v, v' \neq 0$), most of which cannot. Publication 2 reports calculations of all these cross-sections in absolute magnitude from a parameterized model of an intermediate N_2^- ion:



The parameters were calibrated from observations on $v = 0 \rightarrow v = 1$ and $v = 0 \rightarrow v = 2$. The method was given a critical test on the transition $N_2(v=1) \rightarrow N_2(v=2)$, which had not been measured when the calculation was done. (Fig. 1.2/1). The cross-sections for the different channels $v \rightarrow v'$ are given in Figs. 6 and 7 of publication 2.

Publication 2 demonstrates that a parameterized model can be used at a resonance even if the intermediate negative ion is sufficiently long-lived to permit some nuclear relaxation; under these conditions, the "impulse approximation" or "adiabatic approximation" (which was used in publication 1) is not valid.

51.3 Rotational changes of a molecule under electron impact at a resonance : $e + N_2(v=0, J) \rightarrow e' + N_2(v=0, J')$
(Publication 3).

This publication was a joint effort by L. Dubé (supported by the contract) and S.F.Wong. The paper demonstrates that the resonance theory of electron - molecule scattering can account for the changes of rotational state. The paper in fact established that such rotational changes are important, a possibility which had previously been widely questioned. Figure 1.3/1 compares calculated cross-sections for the purely rotational excitation with cross-sections extracted from measurements in which rotational excitation appears as a broadening of the energy distribution of electrons scattered without exciting vibrations.

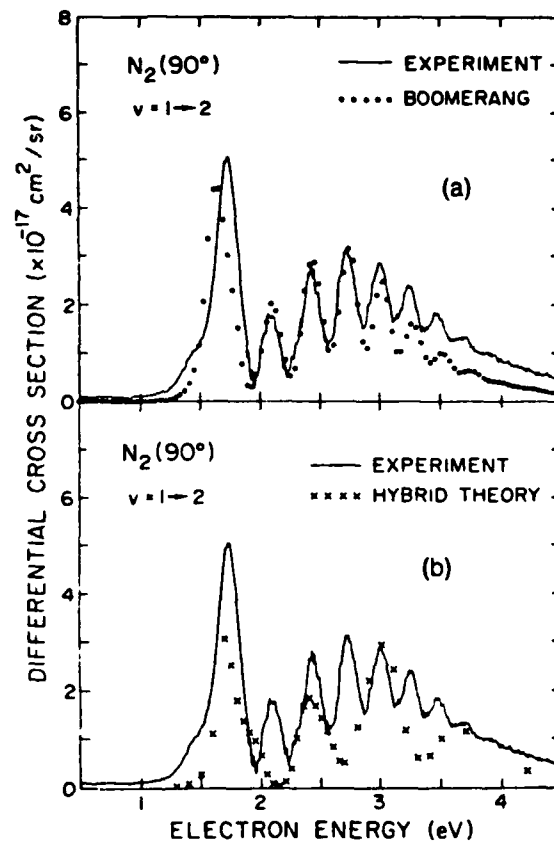


FIG. 4. (a) Differential cross sections at 90° for $v=1 \rightarrow 2$, starting from a vibrationally excited state. Experiment by Wong *et al*; see Ref. 48.: Present theory, from the set of equations listed in the caption to Fig. 2(a), with the parameters listed in column 2 of Table I. (b) $v=1 \rightarrow 2$, at 90° . —: Experiment, as in Fig. 4a. xxxx: "Hybrid theory," Ref. 52.

Fig. 1.2/1 (From publication 2.)

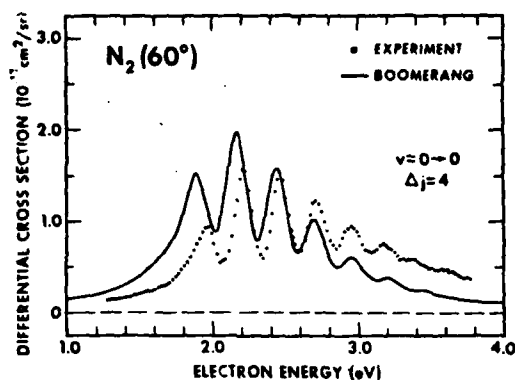


FIG. 6. Comparison of the absolute differential rotational cross sections for $\Delta j=4$ in N_2 as a function of electron energy. The errors in the *absolute magnitude* of experimental cross sections are about 35%. The theoretical calculation is based on the absolute boomerang theory of Dubé and Herzenberg on vibrational excitation, as discussed in Sec. III C.

Fig. 1.3/1. (From publication 3.)

§2.1 Strong vibrational excitation of a polar molecule at a threshold:
 $e + \text{HCl}(v=0) \rightarrow e' + \text{HCl}(v>0)$.
(Publication 4).

Very large vibrational excitation cross-sections, of order 10^{-15} cm^2 , are observed when electrons collide with HCl molecules at energies within 0.5 eV of a vibrational threshold. The effect is important in excimer lasers which use HCl as a source of Cl^- ions from the reaction $e + \text{HCl} \rightarrow \text{H} + \text{Cl}^-$, because the cross-section goes up by one or more orders of magnitude when the HCl target is vibrationally excited. (This observation was reported by Allan and Wong from Yale at the DEAP meeting in Houston in December, 1979).

Publication 4 shows that one should not regard the interaction of an electron with HCl at an impact energy below 1 eV as yet another example of a resonance, because there is no barrier to trap the electron temporarily. A new mechanism, involving a "virtual state", is described, and used to account for the observations, as Figure 2.1/1 shows. This calculation was an essential preliminary to calculations of vibrational excitation and dissociative attachment starting from targets in vibrationally excited states. These cross-sections are needed for the optimization of the XeCl excimer laser; their calculation is now in progress.

§2.2 Dissociative attachment in HCl : $e + \text{HCl} \rightarrow \text{H} + \text{Cl}^-$.
(Reported in conference report 2.)

The importance of this reaction in excimer lasers was explained in §2.1. For reasons explained in publication 4, this reaction is probably not due to the classic mechanism of dissociative attachment, where the electron gets trapped in a resonance behind a potential barrier. The conference report describes a calculation which shows that the available data on HCl molecules in

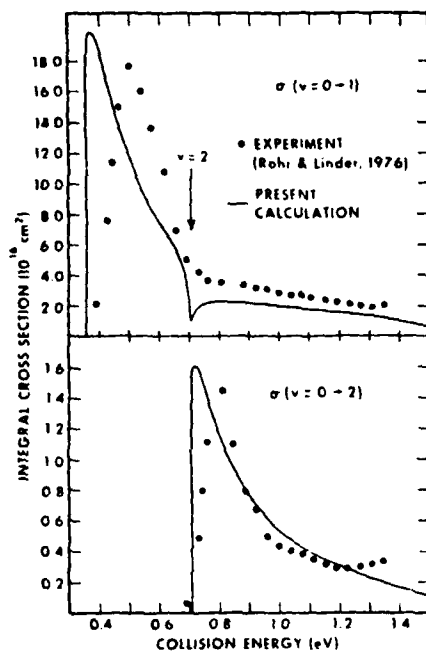
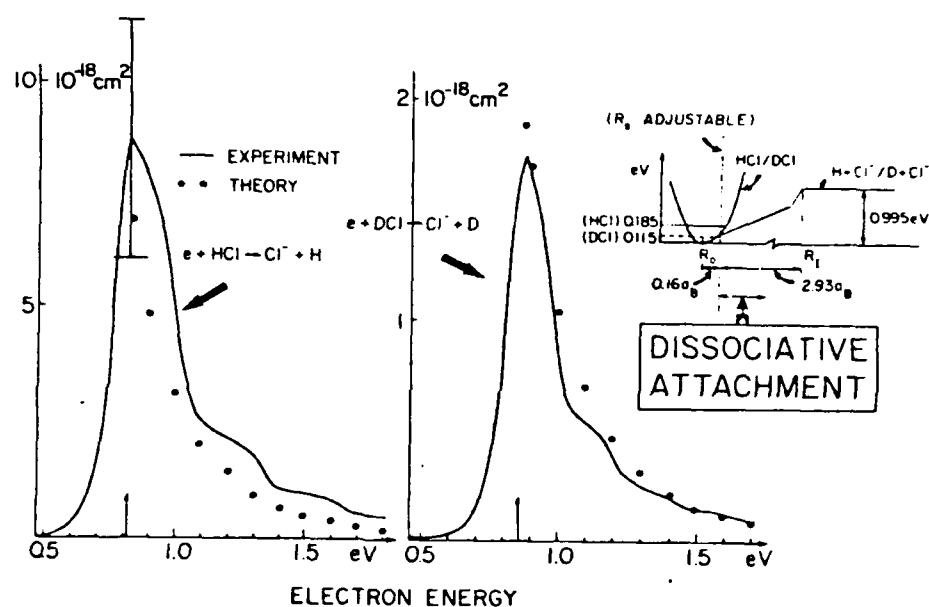


FIG. 1. Vibrational excitation cross sections for electrons on HCl. The experimental resolution is "in the range of 60 meV"; the accuracy of the experimental cross sections is "estimated to about 50% for the threshold peak and to about 20-30% for the rest of the curves." The theoretical curve was calculated for three channels; very similar results were obtained for five channels.

Fig. 2.1/1 (From publication 4.)

since
 ab-initio calculation⁽¹⁴⁾ and a fit⁽¹³⁾ of the observed vibrational excitation both suggest that HCl only barely fails to bind an extra electron, we supposed that the wavefunction of the extra electron outside the molecule has the form $\cos kr/kr$, where k is the momentum. Supposing a bound state of $(\text{HCl})^-$ to be coupled to the function $X_0(R) \cos kr/kr$ by the non-adiabatic coupling between electrons and nuclei (where X_0 is the vibrational ground-state of HCl), we obtained the results shown in Figure 5.



There is one parameter in this calculation: the point R_0 has been adjusted so as to obtain the observed ratio of attachment cross-sections in HCl and DCI; this is possible because attachment occurs in the tail of the initial vibrational state, and this tail has a bigger extent in HCl than in DCI.

The results in Figure 5 are significant because a single adjustable parameter enables one to reproduce four distinct observed features: the absolute magnitudes of the two cross-sections, and the dependence of both on energy near threshold.

Fig. 2.2/1 (From Conference Paper 2.)

their lowest vibrational level are accounted for by a coupling of the incident electron to the velocities of the nuclei. This coupling causes the extra electron to be captured into a bound state $(\text{HCl})^-$ at the nuclear separations where this exists. The calculated results are compared with experiment in Fig. 2.2/1.

2.3 Quenching of excimers by superelastic electron scattering :
 $e + (\text{KrF})^* \rightarrow \text{Kr} + \text{F} + e.$

This is a preliminary estimate to decide whether the rate constant might be high enough for electron-quenching at very high electron-densities ($\approx 10^{16} \text{ cm}^{-3}$) to compete with quenching by collisions with heavy particles. It has been suggested (Greene and Brau, IEEE J. Quant. Elec., 14, 951, 1978) that a rate constant of $10^{-8} \text{ cm}^3 \text{ sec}^{-1}$ would be significant.

We have made an estimate with a model which tends to underestimate the rate constant, and we conclude that a rate constant of $10^{-8} \text{ cm}^3 \text{ sec}^{-1}$ is sufficiently likely to justify a more thorough calculation. The model ignores the coupling of the extra electron with the electronic transition between the two molecular states when the extra electron is inside the molecule. In the final state, the wavefunction of the electron outside the molecule is made to vanish at the molecular surface. This device probably reduces the rate constant by pushing the electron out too much. In the initial state, the wavefunction of the extra electron has a logarithmic derivation at the molecular surface which is varied to explore the sensitivity of the rate constant; this device gives us a range of possible values without the need to do the complicated calculation with the extra electron inside. Outside the molecule, the extra electron feels only a static dipole potential in the initial state.

Figure 2.3/1 shows the rate constants calculated for different logarithmic derivatives in the excited state with Maxwellian electron distributions whose mean energy is indicated on the curves. The rate constant reaches the "important" value of order $10^{-8} \text{ cm}^3 \text{ sec}^{-1}$ over a considerable range of logarithmic derivatives. This result suggests that one should do an ab-initio calculation which removes the arbitrary device of the logarithmic derivatives, and includes the interaction inside the molecule.

§2.4 A prototype reaction of electron detachment in an ion-neutral collision : $\text{H}^- + \text{He} \rightarrow \text{H} + \text{He} + \text{e}$
(Publication 5).

The mechanism of this reaction was not understood because observation yielded a cross-section growing monotonically with ion-energy up to about 2 keV, as Fig. 2.4/1 shows. This behavior conflicts with what one expects from the usual quasistationary state model; there the electronic state becomes auto-ionizing of short nuclear separations, and the probability of detachment decreases with increasing energy because the time the nuclei spend in the detaching region decreases as the speed goes up. The curve for $\text{H}^- + \text{H} \rightarrow \text{H} + \text{H} + \text{e}$ in Fig. 2.4/1 illustrates this traditional model. The publication shows that the observations can be explained by the perturbation of the state of the extra electron by the finite velocity of the nuclei; therefore the cross-section increases with increasing energy. The calculation shows that the model provides a rate of increase of the observed magnitude.

We originally thought that the ion-neutral detachment reaction might be important in excimer lasers, for detachment from F^- and Cl^- ; however, we abandoned the problem when we realized that the slow speeds of the heavy particles in a laser would make the reaction improbable.

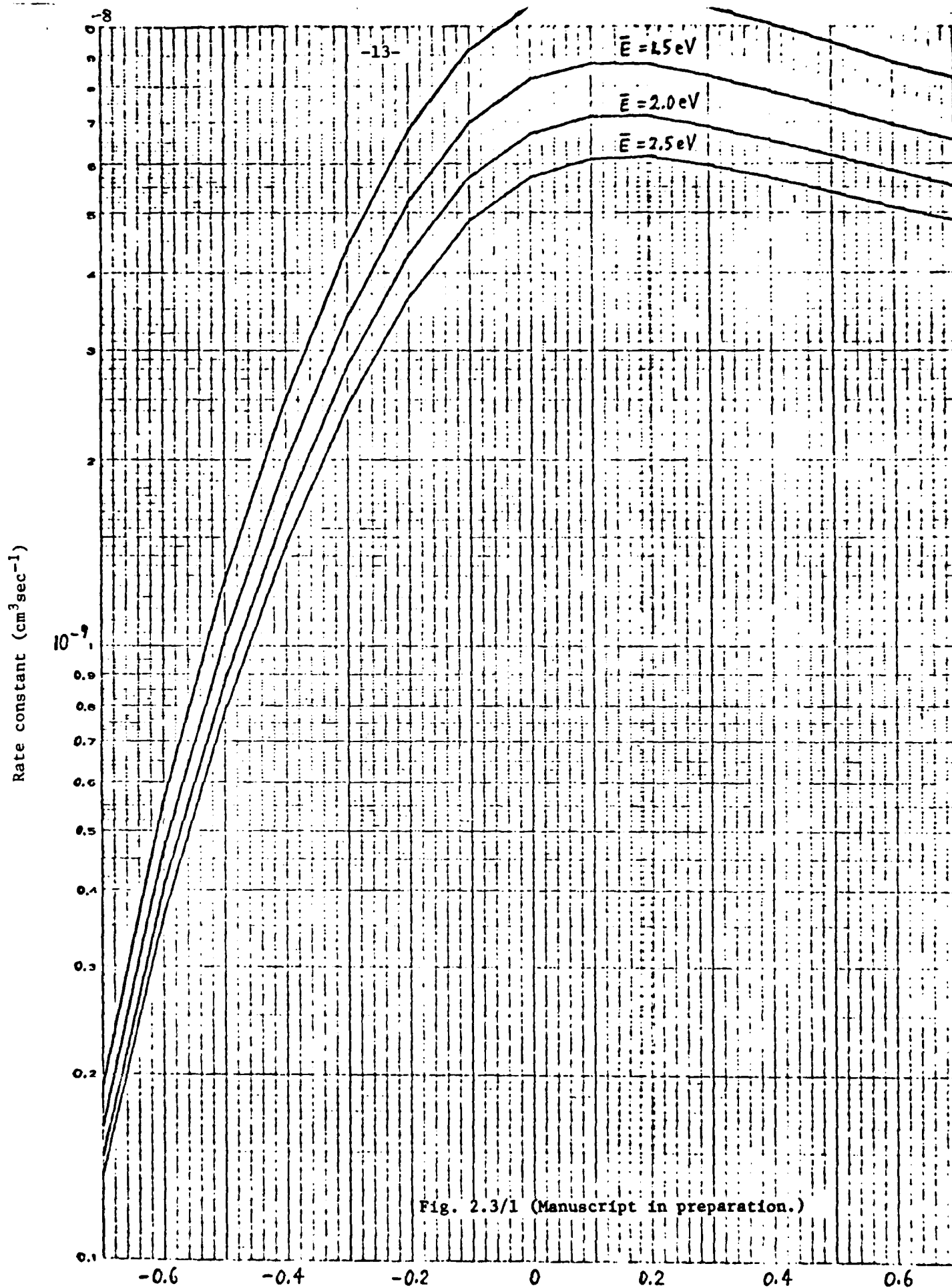


Fig. 2.3/1 (Manuscript in preparation.)

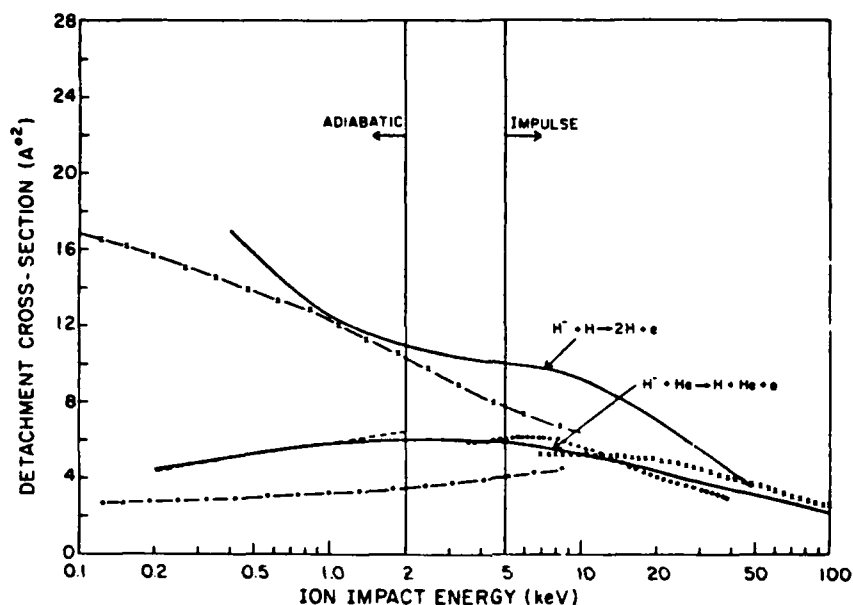


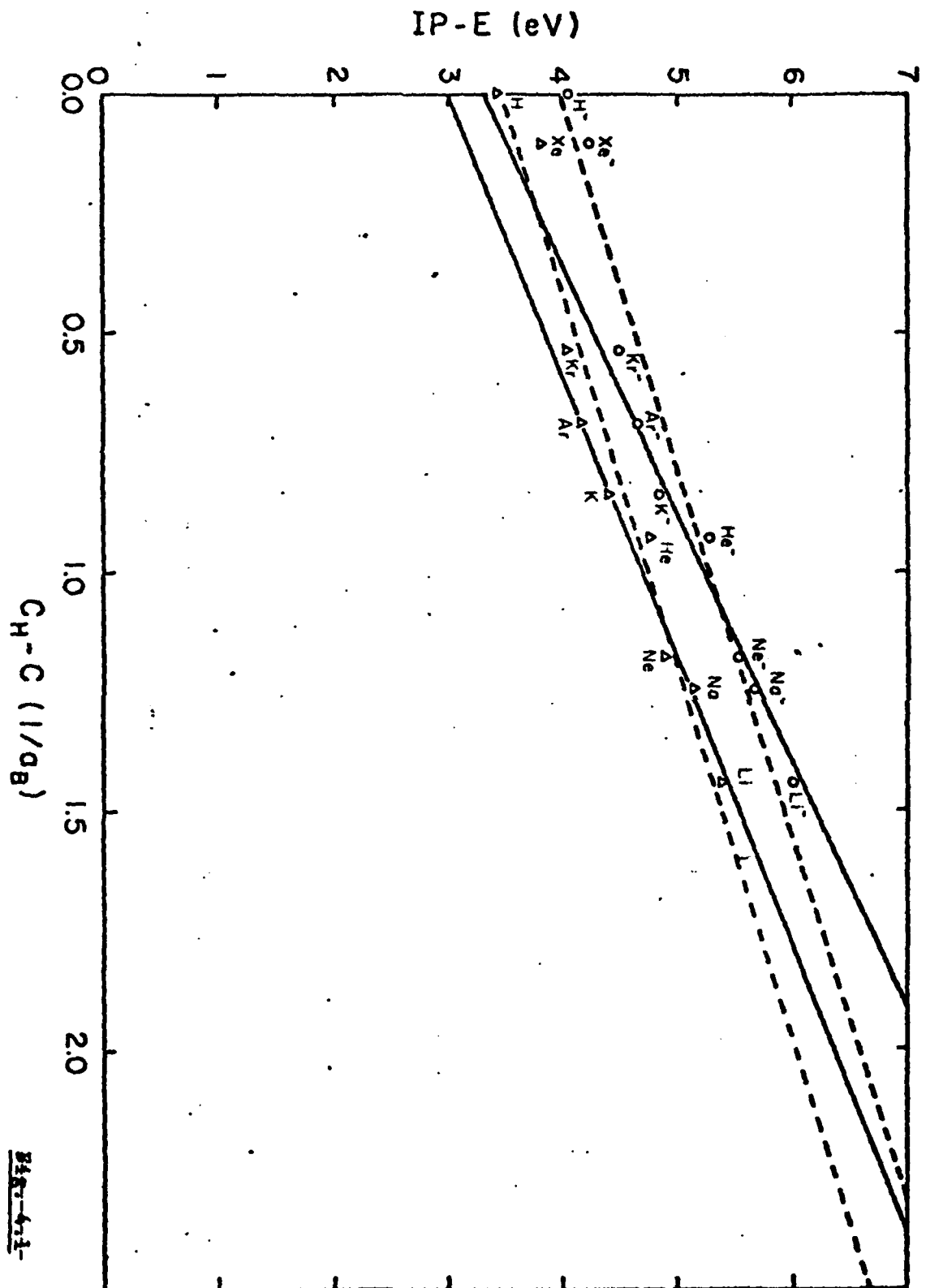
FIG. 4. Electron detachment cross sections. The adiabatic regime is below 2 keV, the impulse regime above 5 keV. —, experiments, from ORNL-5206, in Ref. (2). ·····, impulse calculation, $\text{H}^+ + \text{He}$, Lopantseva and Firsov in Ref. 6. xxxxxx, impulse calculation, $\text{H}^+ + \text{He}$, Bates and Walker in Ref. 6. -X-X-X-X-X, compound state model, $\text{H}^+ + \text{H}$, Ref. 3. -·-·-·-·-, Devdariani, $\text{H}^+ + \text{He}$, Ref. 5. - - - - -, present calculation, $\text{H}^+ + \text{He}$.

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Fig, 2,4/1 (From publication 5.)

§3.1 A test of the grandparent model for electron resonances in collisions with noble gas atoms
(From the Ph.D. Thesis of Piyush Ojha (1980)).

The initial step in the pumping of an excimer laser raises noble gas atoms to their first electronic metastable excited level. The electron impact cross-sections of the excitation step, and of de-excitation collisions, are needed to an accuracy of about 20% for optimization calculations. The cross-sections are dominated by resonances within 2-3 eV of the lowest excitation threshold; these resonances have to be understood before one can calculate cross-sections which are difficult to measure in the laboratory, such as the de-exciting collisions, and collisions which turn metastable levels into radiating states. A popular model of the resonances represents them as two loosely bound electrons in very diffuse orbits outside a positive-ion core; the positive ion is sometimes called a "grandparent". Before using this model to calculate cross-sections, we tested it by showing that it accounts for the energies of resonances about $\frac{1}{2}$ eV below the thresholds. The points in Fig. 3.1/1 are the binding energies of the two outer electrons plotted against a parameter which is essentially a quantum defect of the neutral atom. The binding energy of the outer electron in an excited neutral is also shown. The model demands that the two sets of binding energies should lie on two nearly parallel straight lines (which they do) and predicts the value of the slope. The calculated lines are drawn full; the dashed curves represent a "best fit".



53.2 Excitation cross-sections of noble gas atoms by electron impact, to the lowest metastable and UV emitting levels.
(From the Ph.D. thesis of Piyush Ojha, 1980.)

We have calculated the energies of resonances of the form $(np)^{-1}[(n+1,s)(n+1,p);^3P]$ close to the thresholds of the first excited states of the noble gas atoms (within about 1eV). The excitation cross-sections for the metastable and UV emitting levels in Ne and Ar through these resonances were worked out. The calculation was based on a simple variational wavefunction for the two outer electrons, which was locked to the observed quantum defects at the surface of the positive ion core.

A straightforward interpretation of many of these observed resonances was possible. The cross-section calculation was most successful in $e + Ne$ (Fig. 3.2/1). Similar calculations on $e + Ar$ did not show quite such good agreement with experiment, but did show that the absolute cross-sections for metastable excitation in Argon given by Eggarter (J. Chem. Phys. 62, 833, 1975) are likely to be correct within a factor 2 up to about 1/2 eV above threshold.

Most of the time was spent on Argon. During a 3-month extension of the contract, to February 15, 1980, the calculation of resonance energies was extended to Ne, Kr, and Xe, and the calculation of cross-sections to Neon. Further details of these calculations are available in Piyush Ojha's thesis, and will be sent on request.

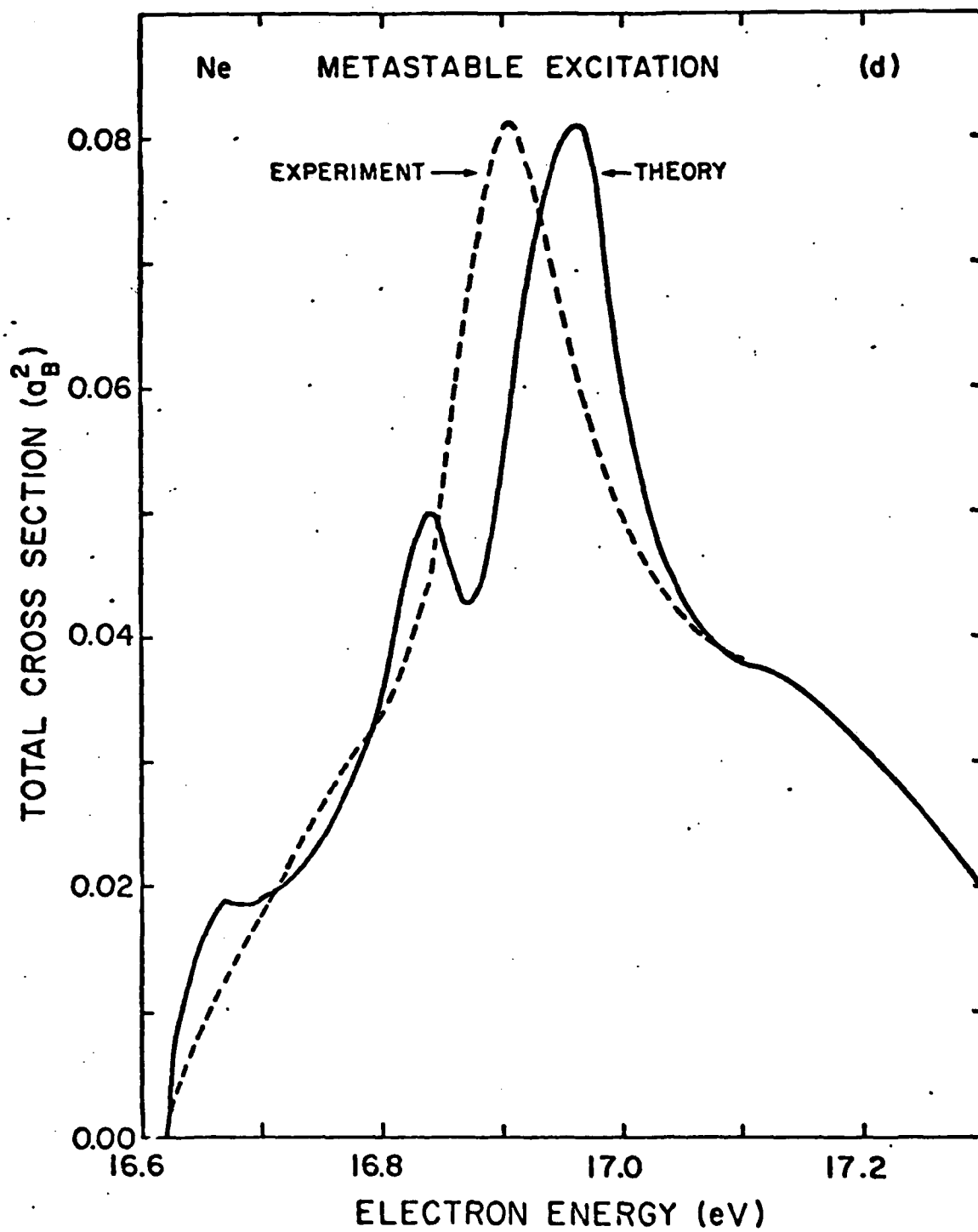


Fig. 4.7

Fig. 3.2/1 (From the Ph.D. Thesis of P. Ojha.)

Publications under the contract

- Publication 1. "Resonant electron-molecule scattering : The impulse approximation in N_2O ". L. Dubé and A. Herzenberg, Phys. Rev. A, 11, 1314, 1975.
- Publication 2. "Absolute cross-sections from the "boomerang model" for resonant electron-molecule scattering". L. Dubé and A. Herzenberg, Phys. Rev. A, 20, 194, 1979.
- Publication 3. "Rotational Excitation of N_2 by Electron Impact : 1-4eV", S.F. Wong and L. Dubé, Phys. Rev. A, 17, 570, 1978.
- Publication 4. "Vibrational Excitation of Polar Molecules by Slow Electrons : HCl". L. Dubé and A. Herzenberg, Phys. Rev. Lett., 38, 820, 1977.
- Publication 5. "Electron detachment in collisions of negative ions : $H^- + He$ ". A. Herzenberg and P. Ojha, Phys. Rev., 20, 1905, 1979.

Invited Conference Papers

- (1) "Strong excitation of nuclear motions in electron-molecule collisions". In the Proceedings of the 10th ICPEAC, Paris, July 21-27, 1977, Invited Papers and Progress Reports, G. Watel (ed.).
- (2) "The two mechanisms for detachment in the adiabatic regime". In the Proceedings of the 11th ICPEAC, Kyoto, Aug. 29-Sept. 4, 1979, Invited Papers and Progress Reports (N. Oda and K. Takayomagi, eds.)
- (3) "Resonances in Vibrational Excitation - Theoretical Studies". In "Symposium on Electron-Molecule Collisions" (Univ. of Tokyo, Sept. 1979) Invited Papers (I. Shimamura and M. Matsuzawa, eds.)

Graduate Student Careers

- Louis Dubé: Ph.D., January 1978.
Became a postdoc at Harwell in England and is
now an assistant professor of physics at
Freiburg in Germany.
- Piyush Ojha: Ph.D., January 1980.
Now a postdoc with D.R.Bates of the Department
of Applied Mathematics, Queen's University,
Belfast, Northern Ireland.

Resonant electron-molecule scattering: The impulse approximation in N_2O

L. Dubé and A. Herzenberg

Department of Engineering and Applied Science, Yale University, New Haven, Connecticut 06520

(Received 4 November 1974)

N_2O is a linear triatomic molecule. Electron scattering shows a $^2\Sigma^+$ shape resonance at ~ 2.3 eV. The lifetime turns out to be so short, 0.9×10^{-15} sec, that one has an impulse picture, in which the nuclei acquire velocity but suffer little displacement during the residence of the projectile electron. The nuclear wave equation at the resonance is solved in the impulse approximation, and is shown to give a good account of the excitation of more than 20 vibrational states observed by Azria, Wong, and Schulz.

I. INTRODUCTION

When a molecule captures an electron to form a short-lived negative ion¹ whose potential-energy surface has a local minimum sufficiently deep to prevent dissociation, the nuclei can move in different ways which depend² on the ratio of the vibrational period ($\approx 2\pi/\omega$) and the decay rate ($\approx \langle \Gamma \rangle / \hbar$).^{2a} If $\omega \gg \langle \Gamma \rangle / \hbar$, one may speak of a "compound molecule" with well-defined vibrational levels; if $\omega \ll \langle \Gamma \rangle / \hbar$, one may speak of an "impulse limit"; and in the intermediate case $\omega \approx \langle \Gamma \rangle / \hbar$, one may speak of a "boomerang model." Each case has its own characteristic and easily recognizable energy dependence in the cross sections; examples of all three are listed in Refs. 2-4.

Detailed discussions of several examples of the "boomerang model" have recently been given.⁴ In this paper, we discuss an example of the "impulse limit," a resonance observed^{5,6} in the collision



at an impact energy of 2.3 eV.

This paper continues the discussion of a model of molecular negative ions in which a complex energy is associated with the electronic state⁷; the imaginary part is proportional to the rate of emission of the extra electron. The complex energy is used as an adiabatic potential in a wave equation for the nuclei (see Sec. III). This model has now been used to discuss vibrational⁸ and rotational⁹ excitation, dissociative attachment,¹⁰ and electron detachment¹¹ and associative detachment¹¹ in ion-molecule collisions.

We shall have to make several approximations; they will be introduced as they are needed, and are then listed again together in Sec. X.

II. STRUCTURE OF THE TRANSIENT OF N_2O^- ION

The observed cross sections in the collision $e + N_2O$ at ≈ 2.3 eV show a smooth hump without fine structure (see Figs. 1 and 2). This contrasts with a

great deal of fine structure observed at some other resonances, for example, a resonance at 3.8 eV in the collision $e + CO_2$.⁴ Such fine structure is a consequence of reflected components in the nuclear wave function in the negative ion, arising at the turning points in the potential-energy surface; these reflected components combine with the nuclear wave produced on capture of the incoming electron to yield an interference pattern which changes with the energy. Consequently, the amplitudes for the production of final states, which are proportional to the overlap integrals of the interference pattern with the final nuclear wave function, oscillate as a function of energy. The absence of such oscillations in the N_2O resonance at ~ 2.3 eV implies that there can be no significant reflected components in the nuclear wave function of the negative ion.

There are two possible reasons for the absence of the reflected components. The first possibility is that the lifetime against reemission of the extra electron is very short. (This would be the only possibility in an ion whose potential-energy surface possesses a minimum stable against dissociation into heavy fragments.) The second possibility is that the ion may dissociate into heavy fragments before reflected components can arise; this could happen in N_2O^- because the threshold for dissociative attachment, $e + N_2O \rightarrow N_2 + O^-$, lies well below the resonance energy of 2.3 eV (at 0.3 eV for a target molecule in its vibrational ground state).

To interpret the experiments, we have made the hypothesis that the first possibility holds in N_2O^- , and verified that the parameter values we need for a good fit of the observations are consistent with the hypothesis. The parameter values have to satisfy two tests: First, the autoionization rate $\Gamma(\bar{R}_e)/\hbar$ for the extra electron in the neighborhood of \bar{R}_e , the equilibrium configuration of the target molecule, has to be large compared with the time for a significant displacement of the nuclei [we may take this time to be of the order of $\frac{1}{2}(2\pi/\bar{\omega})$, where $\bar{\omega}$ is a typical vibrational angular frequency and

Absolute cross sections from the "boomerang model" for resonant electron-molecule scattering

L. Dubé and A. Herzenberg

Department of Engineering and Applied Science, Yale University, New Haven, Connecticut 06520

(Received 30 August 1978)

The boomerang model is used to calculate absolute cross sections near the ${}^2\Pi_g$ shape resonance in e - N_2 scattering. The calculated cross sections are shown to satisfy detailed balancing. The exchange of electrons is taken into account. A parametrized complex-potential curve for the intermediate N_2^- ion is determined from a small part of the experimental data, and then used to calculate other properties. The calculations are in good agreement with the absolute cross sections for vibrational excitation from the ground state, the absolute cross section $v = 1 \rightarrow 2$, and the absolute total cross section.

I. INTRODUCTION

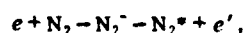
A. Objective

Perhaps the most thoroughly studied of all resonances in electron-molecule scattering at energies of a few electron volts occurs at about 2 eV in e - N_2 collisions.¹ It plays a major role in the pumping of the CO_2 - N_2 laser,² and in the slowing of electrons and the transport of energy in the upper atmosphere.³ The resonance arises from the temporary capture of an electron into the lowest vacant orbital in the N_2 molecule; it is a "shape resonance," in the sense that the target molecule provides a potential well, but does not become excited (except for a minor polarization). The extra electron enters and departs by tunneling through a barrier due to a centrifugal potential.

Up to now, almost all observations on the 2-eV resonance in e - N_2 scattering experiments have dealt with inelastic processes, the excitation of vibrations,⁴ and rotation.⁵ Recently, it has become possible⁶ to detect *superelastic* collisions, in which the energy of the bombarding electron increases by a vibrational quantum. Despite the absence of measurements, the cross sections are often needed in calculations on gas lasers⁷ and in atmospheric processes.⁸ The cross sections may be calculated⁹ with the "boomerang model," which corresponds to a lifetime of the transitory N_2^- ion so short that the nuclei have time for only a single vibrational cycle before the extra electron departs. The object of this paper is to present new calculations with the boomerang model on both superelastic and inelastic processes in the resonance region. The cross sections are given in absolute magnitude. Comparison with experiment confronts absolute measured cross sections with absolute calculated cross sections. The theoretical discussion is restricted to the e - N_2 resonance; only minor changes are needed to modify the theory for other resonances.

The present calculations are an extension of

earlier calculations⁹ on the reaction



which fitted the energy dependence of the observed cross sections for the excitation of the lowest seven vibrationally excited states of N_2 from the ground state, but did not give the absolute magnitude; that calculation was based on a parametrized potential-energy curve for the N_2^- ion. The permissible values of all but one of the adjustable parameters are tied down almost completely by an *ab initio* calculation.¹⁰ The one remaining parameter is a "correlation energy," which Krauss and Mies¹⁰ adjusted to get the resonance appearing at the right energy. It turned out in Ref. 9 that the potential parameters needed to fit the observed cross sections are in excellent agreement with the *ab initio* calculation of Krauss and Mies, if their chosen value of the correlation energy was used. There are some differences in notation between this paper and Ref. 9; they are explained in the Appendix.

B. Observations

The e - N_2 resonance was observed first in measurements of the total cross section,¹¹ with energy resolution too poor to observe vibrational structure. The first measurement with energy resolution good enough to detect vibrational structure and to record the excitation of individual vibrational states were done by Schulz¹² in 1962. Further measurements of vibrational excitation in $e + N_2$ scattering near 2 eV were published by Schulz¹³ and by Ehrhardt and Willmann.¹⁴ The experimental situation has been reviewed by Schulz,¹ most recently in 1976.

Measurements of the total cross section which detect vibrational structure have been done by Golden¹⁵ and by Bonham and Kennerley.¹⁶

Rotational excitation of N_2 by electron impact: 1-4 eV

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Rotational and rotational-vibrational ($v = 0 \rightarrow 1$) excitation in N_2 have been studied with a crossed-beam electron-impact apparatus. In the energy range 1-4 eV, the elastic and vibrational energy-loss peaks show large rotational broadening compared with the apparatus profile (full width at half-maximum, 18 meV). The branching ratios for rotational transitions with $\Delta j = 0, \pm 2, \pm 4$ are obtained with a line-shape analysis applied to the energy-loss profiles. The results for rotational-vibrational excitation at 2.27 eV and scattering angles 30° - 90° are in good agreement with the calculations using the resonant $d\pi$ waves and the rotational impulse approximation. The corresponding results for pure rotational excitation show that the branches with $\Delta j = \pm 2$ and ± 4 are predominantly excited via resonances, while the branch with $\Delta j = 0$ contains a large contribution from direct scattering. The absolute rotational cross sections for $\Delta j = \pm 4$ are measured; they exhibit a large magnitude (10^{-16} cm²) and peak and valley structures in the 1-4 eV range, reminiscent of well-known resonant vibrational excitation. The energy dependence and the absolute magnitude of the rotational cross sections for $\Delta j = \pm 4$ can be understood in terms of a "boomerang" calculation. A comparison of the experiment with the relevant theoretical calculations is made.

I. INTRODUCTION

Rotational and vibrational excitation are the major inelastic scattering processes in low-energy electron impact on molecules. In addition to a fundamental interest, these energy-loss mechanisms also play a dominant role in gas discharges.¹ Whereas there exist extensive measurements on vibrational cross sections,² the direct study of rotational cross sections have been confined^{3,4} to H_2 and D_2 because of the high resolution required to resolve rotational transitions in most molecules.

In N_2 , rotational cross sections at low electron energies have been theoretically studied by various approaches.⁵⁻⁷ There seems to be a general agreement on the dominant role of the $^2\Pi_g$ shape resonance on rotational excitation in the energy range 1-4 eV with selection rules on rotational quantum number $\Delta j = 0, \pm 2$, and ± 4 . The magnitude of the calculated cross sections, however, strongly depends on the approach. The peak cross sections calculated for $j = 0 \rightarrow 4$ transition near 2.3 eV vary^{6,7} from 2×10^{-15} to 3×10^{-17} cm².

We present in this paper a crossed-beam study of rotational excitation in N_2 with an apparatus resolution of 18 meV [full width at half-maximum (FWHM) of energy-loss peaks]. The absolute rotational-vibrational ($v = 0 \rightarrow 1$) cross sections are determined for the $\Delta j = \pm 4$ branches in the 1-4 eV range. As will be seen in Sec. III A, the present apparatus resolution is much larger than the energy spacing of adjacent rotational lines (1 meV for $\Delta j = 2$ and 2 meV for $\Delta j = 4$) but comparable to that of adjacent rotational branches (at 300°K, 8.5 meV between $\Delta j = 0$ and $\Delta j = 2$; 19 meV between $\Delta j = 0$

and $\Delta j = 4$). For large values of j , the branches with $\Delta j = \pm 4$ are separable from the branches with $\Delta j = 0$ and ± 2 . Hence, direct measurement of the energy dependence for $\Delta j = \pm 4$ is possible. The cross sections are made absolute with the help of the experimentally determined elastic and vibrational cross sections and the corresponding branching ratios. For the latter quantities, a numerical line-shape analysis is applied to the energy-loss profiles to extract the relative contribution of all rotational branches. While the branching ratios for the $v = 0 \rightarrow 1$ excitation have been theoretically studied by Read⁸ and experimentally verified by Comer and Harrison,⁹ the present approach using numerical analysis does not rely on the assumption of pure resonant scattering; hence, it is more general and is particularly applicable to the rotational excitation addressed in this work.

II. EXPERIMENT

A schematic diagram of the crossed-beam electron spectrometer is shown in Fig. 1. It is a modified version of the apparatus used by Boness and Schulz.¹⁰ The operation and modifications³ have been previously discussed, therefore only a brief description is given here.

The electron spectrometer consists of an electron monochromator, a molecular beam, and an electron-energy analyzer. Electrons emitted from a thoriated-iridium filament are collimated and focused (electrodes A to L1) onto the entrance focal plane of the hemispherical analyzer of the monochromator. The energy-dispersed electron beam is refocused by this analyzer onto its exit focal plane. With proper adjustment of the exit

Vibrational Excitation of Polar Molecules by Slow Electrons: HCl⁺

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Shape resonances cannot explain the strong vibrational excitation observed in the impact of electrons on polar molecules at threshold, because an important *s*-wave component in the wave function inhibits trapping. We explain the main features observed in HCl by invoking the concept of a virtual state to account for an enhancement of the wave function of a slow departing electron.

Very large cross sections ($\sim 10^{-15}$ cm²) have recently been observed for electrons exciting vibrations in polar molecules near the lowest vibrational threshold.^{1,2} Within 0.5 eV of the thresholds, the observed cross sections are larger by factors of 10–100 than estimates with Born's approximation.³

Up to now, the dominant mechanism for vibrational excitation of molecules by electron impact at energies below 10 eV has been thought to be temporary trapping of the incoming electron in a compound state at a shape resonance.⁴ However, the shape resonance mechanism cannot explain the large vibrational excitation cross sections observed at thresholds^{1,2} because in this case there can be no trapping within a centrifugal potential barrier, as at an electron shape resonance in a molecule. Such trapping is impossible because the angular distributions suggest a strong *s* wave,^{1,2} through which an electron can escape without having to tunnel through a centrifugal barrier.

In HCl, the total cross section near the threshold for the excitation $v = 0 \rightarrow v = 1$ (where v is the

vibrational quantum number) shows a peak about 0.2 eV wide¹; at the peak, the cross section (integrated over scattering angles) reaches 2×10^{-15} cm² (see Fig. 1). At the next threshold, there is a similar but smaller peak for $v = 0 \rightarrow v = 2$, but none for $v = 0 \rightarrow v = 1$.

We have considered how the threshold peaks might arise from an enhancement of the wave function of a very slow departing electron at the molecule. Consider first a fictitious molecule which is roughly spherically symmetric, and whose potential vanishes outside a radius r_0 of molecular dimensions. Let the final state $\psi_f(r, k)$ be an *s* wave, normalized so that its incoming part as $r \rightarrow \infty$ is $(-i) \exp[-i(kr + \delta_f)] / (2ikr)$, where r is the distance of the electron from the mass center, k is the wave number, and δ_f is the phase shift. ψ_f is defined for an electron in the potential from a molecule with nuclei frozen at their equilibrium positions. One finds $\psi_f(r_0, k = 0) = 1 - a/r_0$, where a is the scattering length.⁵ The corresponding amplitude for the free incident wave is 1, so that strong enhancement of the amplitude [i.e., $|\psi_f(r_0,$

Electron detachment in collisions of negative ions: $H^- + He$

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Contrary to the expectation from a compound-state model, observation shows that the detachment cross section increases with energy in the "adiabatic" region below 2 keV. The compound-state model is not appropriate because a strong s-wave component in the wave function allows the extra electron to run away as soon as its state becomes unbound. The detachment cross section increases with collision velocity because detachment is induced by a breakdown of the Born-Oppenheimer approximation, which shifts to larger separations of the nuclei as the collision velocity increases.

I. INTRODUCTION

Risley and Geballe have pointed out¹ a conflict between the observations on the process $H^- + He \rightarrow H + He + e$ and a resonance (or quasistationary-state) model at collision energies below 2 keV, where an adiabatic model might be appropriate. The cross section is observed^{1,2} to rise with the energy of the incoming H^- ion from 0.2–2 keV (Fig. 1), whereas a resonance model predicts a fall as the energy increases.³ A fall is indeed observed⁴ in another detachment reaction, $H^- + H \rightarrow H + H + e$, as the energy of the incoming H^- rises from 0.4–2 keV. This cross section too is shown in Fig. 1. As Risley and Geballe (discussing $H^- + He$) put it: "The fundamental behavior of the detachment cross section in the adiabatic approximation is that the cross section . . . either remains constant with increasing collision energy or monotonically declines. . . . Clearly some

other process is dominating the collision." The object of this paper is to describe another process.

Our analysis of the collision $H^- + He$ starts from assumptions and arrives at conclusions which are closely related to the work of Devdariani^{5(a)}; building on an earlier paper by Demkov,^{5(b)} he successfully obtained a calculated cross section which increases with energy up to a few keV. We differ in the approximation used for the wave function for the extra electron, and in the method of solution of the Schrödinger equation. Devdariani's approximation makes the binding energy grow without limit at large nuclear separations, whereas our approximation makes the binding energy tend to a constant. The two approaches are compared in Sec. V.

At higher energies, from 5 keV upwards, the velocity of the nuclei is too large for an adiabatic model to be appropriate. Here the observed de-

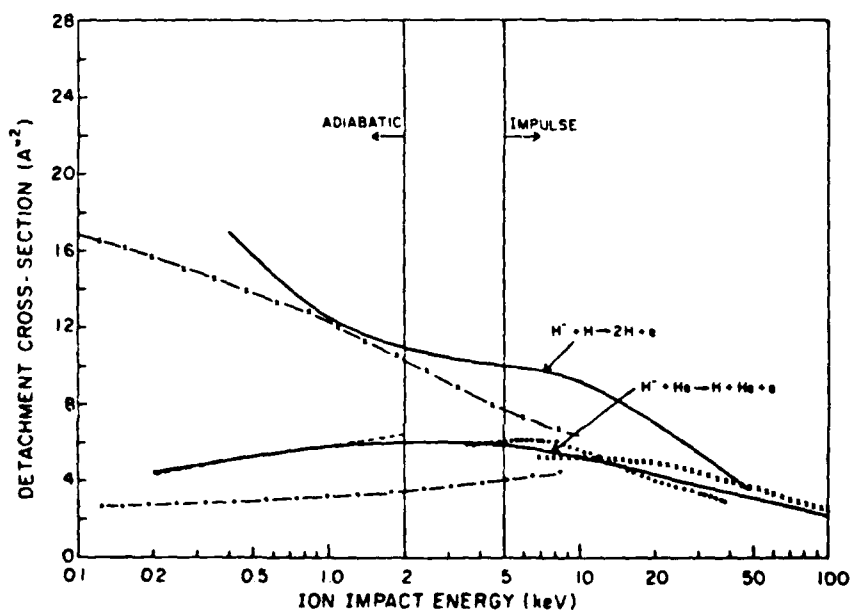


FIG. 1. Electron detachment cross sections. The adiabatic regime is below 2 keV, the impulse regime above 5 keV. —, experiments, from ORNL-5206, in Ref. (2). . . ., impulse calculation, $H^- + He$, Lopantseva and Firsov in Ref. 6. xxxxxx, impulse calculation, $H^- + He$, Bates and Walker in Ref. 6. -X-X-X-X-X, compound state model, $H^- + H$, Ref. 3. -----, Devdariani, $H^- + He$, Ref. 5. - - - - -, present calculation, $H^- + He$.

Conference Paper 1
(X ICPEAC, Paris, 1977; Invited
papers and progress reports.)

STRONG EXCITATION OF NUCLEAR MOTIONS IN
ELECTRON-MOLECULE COLLISIONS

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Vibrational excitation of small molecules by electrons at impact energies of a few eV should, according to the Born approximation, occur with a cross-section of order 10^{-18} cm² if there are no long-range dipole forces involved. Observations by Wong and Schulz in $e + N_2$ at energies from 0 to 30 eV, and by Schulz and Linder near vibrational thresholds of polar molecules, show that there are several mechanisms which yield cross-sections larger than 10^{-18} cm² by several orders of magnitude.

The best-known of these mechanisms are shape resonances, where the electron is trapped temporarily inside a centrifugal barrier. Although the time-dependence of this mechanism cannot yet be investigated with electron pulses, the nature of the time-delay has recently been demonstrated by Rousseau and his co-workers in a scattering experiment on a pulse of laser light. In electron-molecule scattering, recent experiments by Wong and his co-workers have succeeded in studying scattering off a vibrationally excited state, and so applying a critical test to theories which had been calibrated by scattering off the ground state. The structure of the theories, and the way in which they handle the effect of autodetachment on the nuclear dynamics, have been examined by Favard and Parlant.

A newcomer among mechanisms for strong excitations of molecules by electrons is the excitation of small polar molecules at threshold, a region which has become accessible by advances by Linder in handling very slow electrons at high energy resolution. Trapping within a centrifugal barrier does not seem to be involved. Instead, the wavefunction of the extra electron seems to pile up outside one end of the molecule, in a way which might have interesting effects on angular distributions.

Dissociative attachment involves a change in the nuclear state which is much more violent than vibrational excitation. Favard and her colleagues have studied the theory of dissociative attachment in water. They emphasize the effect of autodetachment in cutting out trajectories which dally on the way to separation because a large part of the energy resides in vibration of the residual molecule.

No discussion of resonant attachment is complete without a consideration of its inverse, electron detachment. The novel features observed in the interaction of slow electrons with polar molecules suggest that one should look at the differences in the mechanisms of detachment from homonuclear and heteronuclear two-atom systems. For example, in the reaction $H + H \rightarrow H + H + e$, at low energies, the sym-

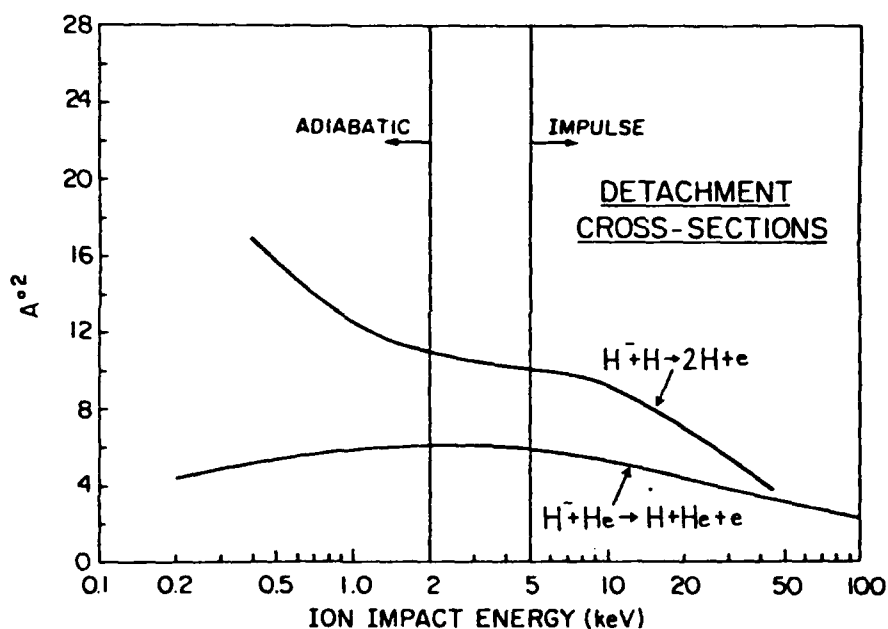
Conference Paper 2
To appear in the book of invited papers and
progress reports, XI ICPEAC, Kyoto, 1979.

THE TWO MECHANISMS FOR DETACHMENT IN THE ADIABATIC REGIME

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Figure 1 shows (1) the cross-sections for the detachment of an electron in the



reactions $H^- + H \rightarrow 2H + e$ and $H^- + He \rightarrow H + He + e$. The H^- ion starts with the laboratory kinetic energy marked on the horizontal axis; the neutral H or He target starts at rest in the laboratory. At an initial laboratory energy of 5.5 keV, the velocity of each nucleus in the CM frame of $H^- + H$ is equal to the root-mean-square velocity of the extra electron in its initial bound state about its own nucleus. We are concerned with the region marked "adiabatic" which corresponds to nuclei moving slowly in comparison to the extra electron. We shall not consider the region marked "impulse", where the nuclei are fast in comparison with the extra electron. The band from 2 to 5 keV has been left, rather arbitrarily, as a transition region.

The two reactions are seen to behave differently in the adiabatic regime; as the energy increases, one cross-section increases, while the other decreases.

Conference Paper 3

77

Symposium on Electron-Molecule Collisions (University of Tokyo, Sept. 1979)
Invited Papers, eds. I. Shimamura and M. Matsuzawa

RESONANCES IN VIBRATIONAL EXCITATION - THEORETICAL STUDIES

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I. INTRODUCTION

This talk deals with the close interaction of an electron with a molecule. Interactions at long range between electrons and polar molecules were reviewed by Takayanagi at ICPEAC in 1975⁽¹⁾. The molecular axes will be regarded as fixed, only the vibrational degrees of freedom being taken into account.

In the absence of a strong distortion of the wave function of an electron striking a molecule at an impact energy of a few eV, one can use the Born approximation to estimate the vibrational excitation cross-section to be of the order of 10^{-18} cm². Therefore processes with substantially larger values of the order of 10^{-16} cm² or more, as at resonances or in threshold peaks, are probes for strong distortions of the wave function out of the initial plane wave.

In section II, we review the possible distortions for the scattering for an electron by a spherical attractive potential well. In the light of this discussion we discuss threshold peaks in vibrational excitation in Section III, and shape resonances in section IV. Feshbach resonances will not be discussed, because they are much less effective than shape resonances in producing vibrational excitation (essentially because the additional excitation and deexcitation of a target electron makes the cross-sections much smaller).

II. SCATTERING BY A POTENTIAL WELL

It is useful to review the distortions of the wave function which can occur in the scattering of an electron off a rigid spherically symmetric potential well. (The coupling to the vibrational degree of freedom will be introduced in sections III and IV).

The potential well has a depth U , of order 1 a.u. (= 27.2 eV), and a range r_0 , of order $2 a_B$. Atomic units will be used, so that the unit of length is the Bohr radius $a_B = 0.52 \times 10^{-8}$ cm, and $\hbar = m = e = 1$.

II.1 Angular momentum $l = 0$

The radial factor in the wave function ψ , multiplied by the distance r from the center of the well, is shown in Figure 1 for three possible values of U . The total energy E is zero in each case, so that $r\psi$ is linear in r when $r > r_0$.

ABSTRACT

ATOMIC COLLISIONS: ELECTRON DETACHMENT AND
RESONANT INELASTIC SCATTERING

PIYUSH CHANDRA OJHA (Ph.D. Thesis)

YALE UNIVERSITY 1980

PART I: Electron Detachment in Collisions of Negative Ions: $H^- + He$

In conflict from the expectation from a compound state model, observation shows that the detachment cross section increases with energy in the adiabatic region below 2 keV. The compound state model is not appropriate because a strong s-wave component in the wavefunction allows the extra electron to run away as soon as its state becomes unbound. The detachment cross section increases with the collision velocity because detachment is induced by a breakdown of the Born-Oppenheimer approximation which shifts to larger separations of the nuclei as the collision velocity increases.

PART II: Metastable and UV Emitting Excitation of Rare Gases in
Collisions with Slow Electrons

A new method is proposed for calculating the positions of resonances and cross sections in electron molecule collisions by enclosing the entire system in a spherical box, thus converting the problem to a bound state problem. It is used to calculate the energies of $[np^5 \ ^2P_{3/2,1/2}] (n+1)s (n+1)p \ ^3P$ resonances in collisions of slow electrons with Ne, Ar, Kr, and Xe. The problem is simplified by invoking the "Grandparent Model" (that the resonances consist of two loosely bound electrons outside a compact positive ion core). The model is tested by explaining the Schulz's Law. Cross sections for excitation of Ne and Ar atoms from the ground state to the lowest metastable and uv emitting levels are calculated.

Collisional Quenching Rate of KrF^* by Low-Energy Electrons
from Electron-Polar Molecule Scattering Theory

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Abstract

One of the mechanisms suggested as being important in the quenching of rare-gas halide metastables in excimer lasers is electronic deexcitation of the metastables by collision with low-energy electrons. In this letter, we calculate cross-sections and rate constants for the process $\text{KrF}(\text{B } ^2\Sigma) + e^- \rightarrow \text{KrF}(\text{X } ^2\Sigma) + e^-$, treating the electron as moving in a dipole potential outside the excimer "core" and taking account of the short-range interactions by parameterizing the logarithmic derivative of the electron radial wave function at the core radius. The results show that rate constants as high as $10^{-8} \text{ cm}^3 \text{ sec}^{-1}$ are conceivable and that close collisions are important in this problem.

First-Order Corrections to the Fixed-Axis Approximation
in Electron-Molecule Scattering

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Abstract

In calculations of electron-molecule scattering where, e.g., the emerging electron is of energy 1 eV or less or the potential has a long-range dipole tail, the fixed-axis approximation may break down. Both of these features figure in the observed vibrational excitation of HCl by low-energy electron impact, and so it would be of interest to estimate the error associated with the fixed-axis calculations that have successfully fit the cross-sections. We derive expressions for the first-order correction to the scattering amplitude and for the corrected differential cross-section which are applicable to the $e+\text{HCl}$ problem. The derivation is based on the Chew-Goldberger formalism for scattering by complex nuclei, and leads to corrections involving the matrix elements of angular momentum operators between exact and asymptotic scattering states.

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